alcohol and carbon dioxide formed approximate to that found
in ordinary alcoholic fermentation.

(6.) When the cell-juice is allowed to act on sugar—either cane-
sugar or dextrose—the quantity of sugar which disappears
is considerably in excess of that which can be accounted for
by the production of carbon dioxide and alcohol.

"On the Thermodynamical Properties of Gases and Vapours as
deduced from a Modified Form of the Joule-Thomson Equa-
tion, with Special Reference to the Properties of Steam." By
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At the present time, the relations between the specific heats and
other thermodynamical properties of gases and vapours, and the devia-
tions from the behaviour of the ideal gaseous substance in isothermal
and adiabatic expansion, remain extremely obscure. The variation
of the latent heat of a vapour, and of its saturation pressure, are
generally expressed by purely empirical formulæ, without theoretical
foundation. Various equations, such as those of Van der Waals, and
Clausius, have been proposed and have been very generally adopted to
represent some of the simplest of these relations, but owing to their
complexity, and to the number of empirical constants involved, their
utility is seriously limited, and the results to which they lead are in
some cases undoubtedly erroneous.

The object of the present paper, which is founded mainly on experi-
ments on steam, is to develop the application of a modified form of the
Joule-Thomson equation, which is sufficiently simple to be of great
value in the discussion of the thermodynamical relations of gases and
vapours, and which leads directly to accurate formulæ for many pro-
perties which have hitherto been represented empirically.

To take the case of steam as an example, all tables of the properties
of steam are at present founded on Regnault's formula for the total
heat H of saturated steam at t C. reckoned from $0°$ C., namely :

$$H = 606 \cdot 5 + 0 \cdot 305t \quad \dots\dots\dots\dots\dots\dots \quad (1),$$

and on his empirical formula for the pressure of saturated steam,
namely :

$$\log p = a + b\mathrm{B}^t + c\mathrm{C}^t \quad \dots\dots\dots\dots\dots\dots \quad (2).$$

The latter formula contains five empirical constants, but it is usual

to employ two different formulæ to cover the range 0°—220° C. of his experiments.

The specific volume of saturated steam, owing to the effects of surface condensation,* cannot be determined by direct experiment, and is generally deduced from the above empirical formulæ, by the application of the well-known thermodynamical relation,

$$L/(v - b) = \theta dp/d\theta \quad\dots\dots\dots\dots\dots\dots \quad (3),$$

where L is the latent heat, v the specific volume of the saturated vapour, and b that of the liquid, θ the absolute temperature, and $dp/d\theta$ the rate of increase of the saturation-pressure with temperature.

Regnault also determined the specific heat of superheated steam at atmospheric pressure by condensing highly superheated steam in a calorimeter; but owing to the small proportion which the superheat of the steam bears to the latent heat, and to the difficulty of calorimetric work at high temperatures, the measurements were not very certain, and many recent experimentalists and writers (*e.g.*, Ewing, Perry, Grindley) have preferred to adopt widely different values deduced by other methods from the formula for the total heat. It was proved by Rankine† that the rate of change of the total heat of steam at low temperatures, at which it very nearly follows the laws of an ideal gas on account of its low pressure and large specific volume, must be very nearly equal to the specific heat of the vapour at constant pressure. Therefore either the specific heat of steam at low temperatures must be 0·305, increasing considerably with the temperature so as to reach the value 0·48 between 100° and 200° C., or else the observations of Regnault must be wrong. In any case it is clear that the variation of the total heat should not be linear, unless we abandon the experimental evidence in favour of the constancy of the specific heat of an ideal gas. It is most likely that the source of the discrepancy is to be found in the difficult calorimetric measurements of the rate of change of the total heat at low temperatures. The determinations of the latent heat by Griffiths, 572·6 calories at 40·2° C., and by Dieterici, 596·7 calories at 0° C.,‡ are from 6 to 10 calories smaller than Regnault's, and imply a rate of change of total heat about 30 per cent. larger, and more nearly equal to the theoretical value. At temperatures above 100° C., the determinations of Regnault are more consistent, but it is very likely, from the method which he employed, that they may be considerably in error. His observations show a sudden increase of six calories above 175° C., which is explained by the discovery and rectification of a leakage of steam through the

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* Ramsay and Young, 'Phil. Trans.,' A, 1892.

† 'Roy. Soc. Edin. Proc.,' 1850.

‡ Griffiths, 'Roy. Soc. Proc.,' December, 1894.

distributing tap into the idle calorimeter. It is clear that he regards the observations above this point with greater confidence. In any case it is unlikely that the order of accuracy attained in his experiments was greater than one-half of 1 per cent. at any point, because his thermometers were not sufficiently perfect, and because it is practically certain from the recent determinations of Reynolds and Moorby of the mean specific heat of water between 0° and 100° C., and from the work of Callendar and Barnes on the variation of the specific heat over the whole range 0° to 100° C., that his value for the specific heat of water at 100° C. is at least 1 per cent. too large. He was also ignorant of the considerable changes which occur in the specific heat of water at low temperatures, and it is evident that his work, though far in advance of his time, requires revision when considered in the light of the great advances which have been made in the last fifty years.

It is obvious from the nature of the problem that the most appropriate method of determining, either the variation of the total heat of steam, or the specific heat of steam, is by the application of some *differential* method, which shall be independent of the determination of the latent heat. In the papers which follow, I have described the application of two such methods to the case of steam. By means of the " Differential Throttling Calorimeter " it is possible, following the method of Joule and Thomson, to determine accurately the variation of the total heat of steam, and the deviations of the specific volume from the ideal gaseous state, in terms of the specific heat at constant pressure. By the " Electrical Method of Measuring the Specific Heat," which is exactly similar to the method already applied* in the case of water, it is possible to determine the specific heat without reference to the latent heat. The details of these experiments are reserved for subsequent communications, the object of the present paper is to explain the thermodynamical relations involved, and to exhibit the calculation of the variations of the specific volume, the specific heats, the total heat, the latent heat, and the pressure of saturated steam in terms of the quantities which are directly observed. The theory of the method is applicable, and has been already applied, to some problems connected with gases, but in dealing with vapours some additions are required, and it is clear that the original equation of Joule and Thomson requires some important modifications.

Modification of the Joule-Thomson Equation.

In order to represent the observations of Regnault on the deviations of CO_2 from Boyle's law, Rankine in 1854 proposed the equation,

$$pv = R\theta - a/\theta v \quad \dots \dots \dots \dots \dots \dots \dots \quad (4).$$

* Callendar and Barnes, 'Brit. Assoc. Report,' 1897 and 1899.

If we write $(v - b)$ for v, on the left hand side, this equation is practically identical, for moderate pressures, with the modified form of the equation of Van der Waals which was devised by Clausius* to meet the objection that the term a/v in the equation of Van der Waals did not satisfactorily represent the variation of the phenomena with temperature. In adopting this equation of Rankine's to represent their observations " On the Thermal Effects of Fluids in Motion,"† Joule and Thomson substituted $v = \mathrm{R}\theta/p$ in the small term $a/\theta v$, which thus became $ap/\mathrm{R}\theta^2$. For the purpose of their observations the modification appeared to be unimportant, and they quote the equation as Rankine's, but it really introduces a great simplification. If we write the equation in the form,

$$v = \mathrm{R}\theta/p - a/\mathrm{R}\theta^2 \quad \dots\dots\dots\dots\dots\dots\dots \quad (5),$$

we observe that the small term is a function of the temperature only, and is independent of the pressure or volume. The isothermals on the p, v diagram are equilateral hyperbolas, identical in form with those of an ideal gas. Or, if we plot the product pv against p, as is usual in considering the deviations of a gas from Boyle's law, the isothermals are straight lines inclined to the axis of p at various angles, which diminish as the temperature rises. It is proved by the experiments of Joule and Thomson, and more clearly by the subsequent observations of Amagat and others, that the equation, even in this simple form, represents a very good first approximation to the deviations of actual gases from Boyle's law at moderate pressures. The approximation holds, for instance, in the case of CO_2, according to the observations of Amagat, up to 50 or 100 atmospheres at temperatures between 100° and 200° C. The application of the equation to the case of vapours may, however, be still further simplified, and rendered at the same time more accurate, by two slight but important modifications.

(1) It is practically certain that the equation of a perfect, or pluperfect, gas at high temperatures is not $pv = \mathrm{R}\theta$, but $p(v - b) = \mathrm{R}\theta$, where b is the minimum volume or " co-volume " of Hirn and Van der Waals. The co-volume b is variously regarded as being equal to four times or $4\sqrt{2}$ times the absolute volume of the molecules. It is relatively small at moderate pressures (about one-thousandth of v at atmospheric pressure), and is often negligible, but may with great probability be taken as equal to the volume of the liquid at temperatures where the vapour pressure is small.

(2) It is usual in the kinetic theory of gases, either tacitly or explicitly, to make the fundamental assumption that the average total kinetic energy of the molecules of a gas, including motions of vibration and rotation, is directly proportional to the kinetic energy of transla-

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* ' Phil. Mag.,' June, 1880.

† ' Phil. Trans.,' 1862.

tion, which is equal to $3pv/2$ per unit mass at any temperature.   It follows from this assumption that the limiting value of the specific heat of a gas in the ideal state ($p = 0$, $v = \infty$), either at constant pressure or at constant volume, must be constant, if the molecule is stable, since it is directly proportional to pv/θ, which tends to a constant limit when $p = 0$, even in the case of vapours at temperatures far below their boiling points.   These constant limiting values of the two fundamental specific heats will be denoted by the symbols $S°$ and $s°$ respectively. As a further simplification we may assume that the kinetic energy of a vapour is proportional to p $(v - b)$ at all stages and not only in the limit. On this assumption it is also necessary to suppose that the index of θ in the small term $a/R\theta^2$ in the Joule-Thomson equation is not 2, but $n = s°/R$, the ratio of the limiting value of the specific heat at constant volume to the limiting value of pv/θ.   If we adopt the hypothesis of Clerk Maxwell with regard to the distribution of energy between the various degrees of freedom of a molecule, which, in the absence of certain knowledge with regard to the exact nature of a molecule, appears to be the only practical working hypothesis, the theoretical value of this limiting ratio should be $1·5$ for a monatomic gas like argon, $2·5$ for a diatomic gas like oxygen or hydrogen, $3·5$ for a tri-atomic gas like steam or CO_2, and so on, increasing by unity for each additional atom in the molecule.   The value $3·5$ for the index is closely verified in the case of steam by the experiments to be described on the Joule-Thomson effect, and also by the experiments on the specific heat, by which this relation was first suggested.

Adopting these two modifications, of which the second is the more important, the equation may be written in the form,

$$v - b = R\theta/p - c°(\theta°/\theta)^n = V - c \dots\dots\dots\dots\dots\dots (6),$$

in which V is taken as a convenient abbreviation for the ideal volume $R\theta/p$, and the co-volume b is taken as constant and equal to the volume of the liquid.   The small correction c, representing the state of co-aggregation of the molecules, is called the "co-aggregation volume," and is a function of the temperature only, varying inversely as the nth power of the absolute temperature, where the index n is used as an abbreviation for $s°/R$.   It is a quantity of the same dimensions as a volume, and is measured in cubic centimetres.   The numerical value of c in the case of steam at $100°$ C. is $26·5$ c.c., as deduced from the experiments on the Joule-Thomson effect and the specific heat.   The calculated value of $c°$ at $\theta° = 273·0°$ is $79·0$ c.c.   It is obvious on the simplest considerations that the co-aggregation volume c cannot remain accurately constant at high pressures, since there is an obvious limit to the possible co-aggregation of the molecules.   If, for instance, the molecules are simply paired, the pairing must cease when $v - b = c$. But it is certain from the differential experiments that the modified

equation represents a very accurate approximation to the facts at moderate pressures, although n is not necessarily equal to $s°/R$ in all cases.

Variation of the Specific Heats.

It would appear at first sight as though the modified equation were more complicated than the original of Joule and Thomson, but it leads as a matter of fact to far simpler relations between the thermodynamical properties, and makes it possible to attack problems which would be quite intractable with the more complicated forms of empirical equations in vogue.

If S and s are the specific heats at constant pressure and at constant volume respectively, and ϕ is the entropy, we have the well-known relations,

$$(dS/dp)_\theta = \theta d^2\phi/d\theta\, dp = -\theta(d^2v/d\theta^2)_p \ \ldots\ldots\ldots\ldots \quad (7),$$

$$(ds/dv)_\theta = \theta d^2\phi/d\theta\, dv = +\theta(d^2p/d\theta^2)_v \ \ldots\ldots\ldots\ldots \quad (8).$$

Assuming the characteristic equation (6), it is easy to prove from these relations that the values of the specific heats at any temperature and pressure are given by the simple formulæ,

$$S = S°(1 + nc/V) = S° + n(n+1)pc/\theta \ \ldots\ldots\ldots\ldots \quad (9),$$

$$s = s°(1 + nc/V)(1 - c/V) \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10),$$

where $S°$ and $s°$ are the constant limiting values of the specific heats when $p = 0$. The ratio of the specific heats $g = S/s$ is given by the relation,

$$g = S/s = S°/s°(1 - c/V) = g°/(1 - c/V) \ \ldots\ldots\ldots\ldots \quad (11),$$

where $g°$ stands for the constant limiting value of the ratio, and is equal to $(n+1)/n$.

Isentropic Relations.

The isentropic relations are greatly simplified by the assumption $n = s°/R$, since in this case the ratio of the co-aggregation volume c to the ideal volume V, or to the difference of specific volumes of the vapour and liquid $v - b$, is constant at constant entropy. From the characteristic equation (6), we have for the isothermal elasticity E_θ and the isentropic elasticity E_ϕ, since $E_\phi/E_\theta = S/s = g = g°/(1 - c/V)$,

$$E_\theta = -v(dp/dv)_\theta = +pv/V \ \ldots\ldots\ldots\ldots\ldots\ldots \quad (12),$$

$$E_\phi = -v(dp/dv)_\phi = +gE_\theta = g°pv/(v - b) \ \ldots\ldots\ldots \quad (13).$$

The equation of the isentropics may therefore be written in the forms—

$$p(v - b)^{g°} = \text{constant}, \quad \text{or} \quad p^n(v - b)^{n+1} = \text{constant},$$

or $\quad p/\theta^{n+1} = \text{constant}, \quad \text{or} \quad (v - b)\theta^n = \text{constant} \ \ldots\ldots\ldots \quad (14).$

The constant value of the ratio c/V along an isentropic is given by the relation,

$$e^{nc/\mathrm{V}}e^{\phi/\mathrm{R}}c/\mathrm{V} = e^{nc^\circ/\mathrm{V}^\circ}e^{\phi^\circ/\mathrm{R}}c^\circ/\mathrm{V}^\circ \ldots\ldots\ldots\ldots\ldots (15),$$

which may be written in the form,

$$c/\mathrm{V} = (c^\circ/\mathrm{V}^\circ)(p/p^\circ)(\theta^\circ/\theta)^{n+1} \ldots\ldots\ldots\ldots\ldots (16),$$

where e is the base of natural logarithms, and the symbols p°, c°, V°, θ°, ϕ°, refer to a standard state such as 0° C., and 760 mm.

Isothermal Expansion.

The Change of Entropy $\phi - \phi^\circ$ in expansion from p° to p at a constant temperature θ° is deduced from the relation,

$$d\phi = (d\phi/dp)_\theta dp = -(dv/d\theta)_p dp = -(\mathrm{R}/p + nc^\circ/\theta^\circ)dp\ldots\ldots (17),$$

whence $$\phi - \phi^\circ = \mathrm{R}\log p^\circ/p + (p^\circ - p)nc^\circ/\theta^\circ \ldots\ldots\ldots\ldots (18).$$

The Heat Absorbed is given by the expression,

$$\mathrm{Q} - \mathrm{Q}^\circ = \mathrm{R}\theta^\circ \log p^\circ/p + (p^\circ - p)nc^\circ \ldots\ldots\ldots\ldots (19).$$

The Work Done, $\mathrm{W} = \mathrm{R}\,\theta^\circ \log p^\circ/p$, is the same as for an ideal gas between the same limits of pressure.

The Change of Intrinsic Energy is, therefore,

$$\mathrm{E} - \mathrm{E}^\circ = nc^\circ(p^\circ - p) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (20).$$

Heating at Constant Pressure.

The Heat Absorbed in a rise of temperature from θ° to θ at constant pressure p° is given by the equation

$$\mathrm{Q} - \mathrm{Q}^\circ = \int \mathrm{S}d\theta = \mathrm{S}^\circ(\theta - \theta^\circ) + (n+1)p^\circ(c^\circ - c)\ldots\ldots\ldots (21).$$

Change of Energy,

$$\mathrm{E} - \mathrm{E}^\circ = s^\circ(\theta - \theta^\circ) + np^\circ(c^\circ - c) \ldots\ldots\ldots\ldots\ldots (22).$$

The Work Done,

$$\mathrm{W} = \mathrm{R}(\theta - \theta^\circ) + p^\circ(c^\circ - c) \ldots\ldots\ldots\ldots\ldots (23).$$

Change of Entropy,

$$\phi - \phi^\circ = \int \mathrm{S}d\theta/\theta = \mathrm{S}^\circ \log \theta/\theta^\circ + np^\circ(c^\circ/\theta^\circ - c/\theta) \ldots\ldots (24).$$

In passing from any one state represented by the co-ordinates p°, θ°, to any other state represented by p, θ, both the change of energy and the change of entropy must be independent of the process by which

the change is effected, and equal to the values calculated by combining isothermal expansion with heating at constant pressure. We thus obtain the following general expressions for the change of energy and the change of entropy in any transformation from the state $p°$, $\theta°$, to the state p, θ :—

$$\mathrm{E} - \mathrm{E}° = s°(\theta - \theta°) - n(pc - p°c°) \;\ldots\ldots\ldots\ldots (25).$$

$$\phi - \phi° = \mathrm{S}° \log \theta/\theta° - \mathrm{R} \log p/p° - n(cp/\theta - c°p°/\theta°)\ldots\ldots (26).$$

These expressions are true for any value of n.

Calculation of the Specific Volume of Saturated Steam.

As an illustration of the numerical application of this method, I propose to take the case of steam, as the most important and interesting. But the methods and reasoning would be equally applicable to any other gases or vapours for which the requisite experimental data were available.

The deviations of the specific volume from the ideal state are immediately given by the values of the co-aggregation-volume c, which are easily calculated. It is quite a mistake to suppose, as is frequently stated, that there is any sudden or rapid change in the co-aggregation as the saturation point is approached. This idea has arisen merely from experimental errors due to surface condensation. Under certain conditions it is well known that the vapour can exist in stable equilibrium at pressures greatly in excess of the saturation value, provided that there is no liquid present, or any nuclei, or other aids to condensation. I have not, for obvious reasons, succeeded in investigating the properties of *supersaturated* steam by the method of throttling; but there does not appear to be any reason to suppose that its behaviour could not be predicted with great probability by assuming that the co-aggregation volume remains constant at constant temperature, which is certainly a very close approximation to the behaviour of steam in the superheated condition down to the temperature of saturation.

In the following table, which contains a few sample values of the co-aggregation c and the specific volume v, the ideal specific volume of steam at 100° C. and 760 mm. pressure is taken as 1698·0 c.c., which is calculated by assuming the density of oxygen, corrected for its probable co-aggregation, and taking the ratio of the molecular weight of steam to that of oxygen to be 18/32. The value of c for steam at 100° C. is taken as 26·5 c.c., and the values at other temperatures are calculated by the formula (6) :—

Table I.—Specific Volume and Co-aggregation of Steam.

Temp. Cent.	Satura-tion-pressure.	Co-aggre-gation. *c.*	Ideal volume. **V.**	Specific volume. *v.*	Co-aggre-gation. Ratio. *c*/**V.**	Deviation. Ratio. (*c* − *b*)/**V.**
° 0	atmos. 0 ·00613	c.c. 79 ·0	c.c. 202680 ·0	c.c. 202602 ·0	0 ·000389	0 ·000385
20	0 ·02323	61 ·7	57370 ·0	57309 ·0	0 ·001076	0 ·001060
40	0 ·0731	49 ·0	19490 ·0	19442 ·0	0 ·002515	0 ·002463
60	0 ·1267	39 ·4	7710 ·0	7671 ·0	0 ·00512	0 ·00498
80	0 ·4670	32 ·14	3438 ·0	3407 ·0	0 ·00932	0 ·00903
100	1 ·0000	26 ·50	1698 ·0	1672 ·5	0 ·01560	0 ·01500
120	1 ·961	22 ·07	911 ·7	890 ·6	0 ·02425	0 ·02305
140	3 ·570	18 ·56	526 ·0	508 ·4	0 ·0354	0 ·0333
160	6 ·01	15 ·74	321 ·7	307 ·1	0 ·0490	0 ·0455
180	9 ·93	13 ·41	207 ·7	195 ·3	0 ·0648	0 ·0594
200	15 ·37	11 ·55	140· 1	129 ·6	0 ·0825	0 ·0742

The values of the specific volume v are calculated for the saturation-pressures, given in atmospheres in the second column. The values for any other pressures can be calculated with equal ease, since the co-aggregation-volume c, which is given in the third column, depends only on the temperature. It is necessary in each case to calculate the appropriate value of the ideal volume $V = R\theta/p$. The values of the specific volume v are found by subtracting $(c - b)$ from the ideal volume. The values of the co-aggregation ratio c/V, and the deviation-ratio $(c - b)/V$, are also given, as the first is useful in calculating the values of the specific heats by formulæ (9), (10), and (11), and the second affords the most convenient means of representing graphically the variations of the specific volume, since it is quite impracticable to plot the specific volume itself on an adequate scale.

Graphic Representation of the Variations of Specific Volume.

The best method of representing these results graphically appears to be that adopted in fig. 1, of plotting the ratio of v/V or $(c - b)/V$ against p. We have—

$$pv/R\theta = v/V = 1 - (c - b)/V = 1 - (c - b)p/R\theta \ldots\ldots (27).$$

Since c is constant at constant temperature, the isothermals are

straight lines inclined at different angles to the axis, but all intersecting at the same point, $v/V = 1$ when $p = 0$. These lines are drawn for each 20° of temperature in the figure, and are all represented as terminating in the saturation curve, although, as a matter of fact, it is
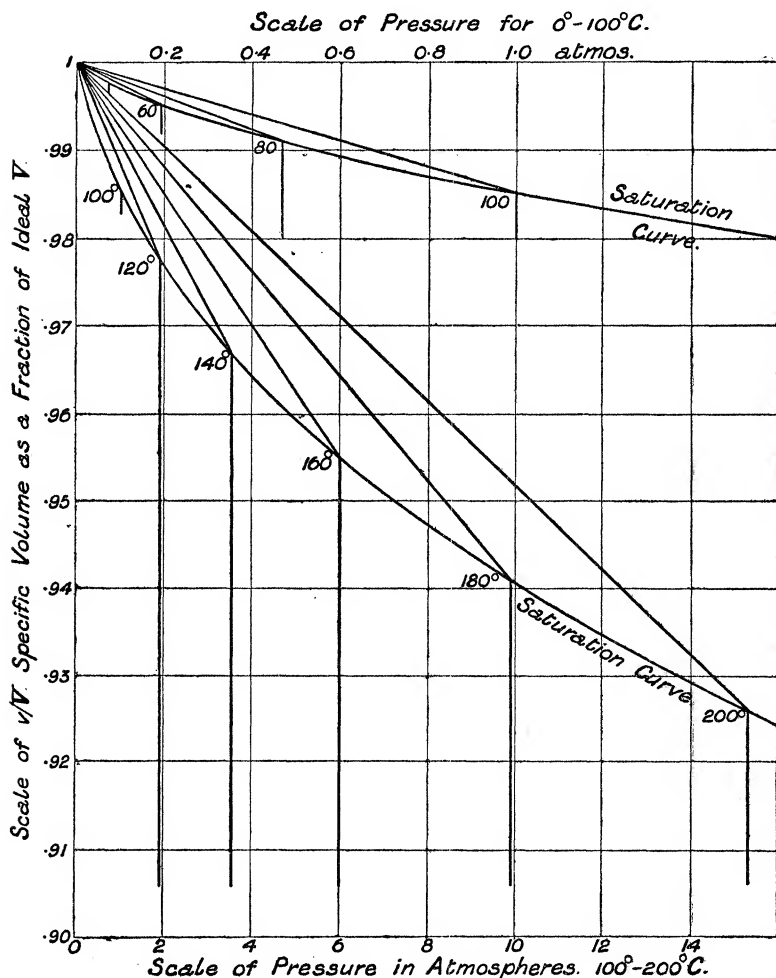

Fig. 1.—Specific volume of steam.

possible to suppose them produced beyond it, if condensation does not occur. The first part of the curve up to 100° C. is represented on a ten times larger scale of pressure in the upper part of the figure. It will be observed that the whole deviation from the ideal volume at 100° C. is only 1·5 per cent. at saturation-pressure. This method of

plotting is analogous to that rendered familiar by Amagat and others in the case of the deviation of gases from Boyle's law. It is usual to plot the product pv against p, but it seems to me to be preferable to plot $pv/\mathrm{R}\theta$ instead of pv, because the pv method confuses the diagram by introducing the effects of the variation of temperature, so that the different isothermals cannot be so well compared, and their relations observed.

In the diagrams of Amagat and others, who have adopted the direct method of measuring the whole specific volume instead of the differential method of observing only the deviation from the ideal volume, the isothermals are not accurately straight, but always bend downwards more steeply as saturation is approached, so that they are concave to the axis of pv. There seems reason to believe that this peculiarity may be partly due to the effect of surface condensation so well established by the observations of Ramsay and Young.* It is true that a similar though smaller increase in the slope results from the work of Natanson on the Joule-Thomson effect for CO_2 at pressures up to 26 atmospheres, at a temperature of $20°$ C. But in that case also the effect may be explained by condensation in the pores of the porous plug, as is indicated in some of the work of Joule and Thomson. I was not able to find by the differential method, which would eliminate any error of this kind, any trace of this effect at moderate pressures. In fact, the cooling effect appeared to diminish very slightly with increase of pressure, as it should, on account of the small increase in the value of the specific heat with increase of pressure. If this is generally true for other vapours, it would appear possible that many of the complications which have been introduced in current forms of empirical equations of the fluid state, may serve only to represent errors inherent in the experimental methods on which they are founded.

Values of the Specific Heats of Steam.

The values of the specific heats at any temperature and pressure are easily calculated from their limiting values at zero pressure, by means of the formulæ (9), (10), and (11) already given. The actual value of the specific heat at a pressure of one atmosphere was experimentally determined by the electrical method to be subsequently described. The value so found, though slightly larger than Regnault's, agreed so well with the theoretical value deduced from the characteristic equation (6) by means of Maxwell's assumption, that there can be little doubt that the method of deduction employed is valid. The value of the constant R for steam is readily found from the value of the ideal volume already assumed, we thus obtain†

* 'Phil. Trans.,' A, 1892.

† Assuming that the pressure due to a column of mercury 760 mm. in height at $0°$ C. and sea-level in latitude $45°$ is equal to 1·0133 megadynes per sq. cm.

$$R = 4.613 \times 10^6 \text{ C.G.S.} = 0.4613 \text{ joule/deg. C.}$$
$$= 0.11037 \text{ cal./deg. C.}$$

The unit of heat adopted in this paper is the thermal capacity of 1 gramme of water at 20° C., which is taken as being equivalent to 4·180 joules, from the mean of the results of Rowland and of Reynolds and Moorby, compared and reduced by the work of Callendar and Barnes on the variation of the specific heat of water over the whole range 0° to 100° C.

The limiting values of the specific heats of steam, and of their ratio, in terms of this unit are as follows,

$$S^° = 0.4966 \text{ cal./deg. C.} \quad s^° = 0.3862 \text{ cal./deg. C.} \quad g^° = 9/7 = 1.2857.$$

In the following table, the values of S, s, and g are given for saturated steam at the point of saturation, in order to illustrate the increase of specific heat with pressure. The values of the specific heat S' at a pressure of one atmosphere at various temperatures are also given, to show the diminution of the specific heat with rise of temperature. The values enclosed in brackets are of course imaginary, but are included to show more clearly the nature of the change. The value of the specific heat at constant pressure has been calculated by Zeuner from Regnault's observations to be 0·568, on the assumption that the specific volume of steam is a linear function of the temperature at constant pressure, in which case the specific heat at constant pressure is independent of the pressure. Another common assumption is that the pressure at constant volume is a linear function of the temperature (Van der Waals). Neither of these assumptions can be reconciled with the most accurate thermometric work at moderate pressures, or with the present experiments on steam by the method of the differential throttling calorimeter. The advantage gained by these assumptions is very slight and one-sided. The partial constancy of one specific heat is a small matter, if at the same time the other thermodynamical relations are rendered so complicated as to make the equations useless. The values of the specific heat of steam at constant pressure have been recently calculated by Grindley from his throttling experiments,* assuming the linear formula (1) of Regnault for the Total Heat of steam. These values are included in Table II for comparison. The numbers given in brackets are not given by Grindley, but are calculated by an extension of his method to show the effect of his hypothesis. The extraordinary differences between his values and mine, as shown in the adjacent columns (6) and (7) of Table II, are not due to any discrepancy in our experiments, but simply to his assumption of Regnault's formula for the total heat. The method of deducing the specific heat from the total heat, though it has often been applied, is unsound in principle, because the specific heat

* 'Phil. Trans.,' A, vol. 194, 1900, pp. 1–36.

depends on the rate of variation of the total heat, so that all the errors in the formula for the total heat are enormously exaggerated in the calculation of the specific heat.

The last column in the table contains the values of the so-called "Specific Heat of Saturated Steam," *i.e.*, the value of the specific heat when $dp/d\theta$ is determined by the condition that the steam is to remain saturated. The value in this case is given by the formula

$$S \text{ (sat.)} = d\text{H}/d\theta - \text{L}/\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots (28),$$

which is most readily obtained by differentiating the expression for the entropy of saturated steam, namely, $\phi_s = \phi_w + \text{L}/\theta$, where ϕ_w is the entropy of water reckoned from $0°$ C. The values of S (sat.) also differ considerably from those which have been previously calculated on the usual assumption that $d\text{H}/d\theta$ is constant, and equal to $0\cdot305$, as in formula (1).

It will be observed that the mean value of the specific heat of steam at a constant pressure of one atmosphere between the limits $120°$ and $200°$ C., the range of Regnault's experiments, is $0\cdot512$ according to the values given in Table II. This value is not so greatly in excess of the value $0\cdot48$ given by Regnault as to be beyond the limits of experimental error, especially if we consider that the method which he adopted must necessarily have given rise to constant errors in defect, and that the superheat was only one-sixteenth of the total heat to be measured.

It is probable that the variation of the specific heats of all other gases and vapours, to which the Joule-Thomson equation can be applied, is of the same type as that exhibited above in the case of steam. I have succeeded in reconciling a good many of the apparently discordant experimental data on the subject by means of this hypothesis, but the experiments themselves are difficult, and the question of the variation of the specific heats of gases is obscured by unavoidable errors. Among the most remarkable and accurate of recent results are those of Joly on the specific heats of Air and CO_2 at constant volume, determined by means of his differential steam-calorimeter. The values which he obtained are much larger than those deduced from Regnault, and cannot be reconciled with them on the common assumption (Van der Waals) that the specific heat at constant volume is constant, but they agree remarkably well, considering the difficulty of the experiments, with the theory proposed in this paper. A fuller discussion of these and similar relations will be reserved for a future communication.

Table II.—Specific Heats of Steam.

Temp. Cent.	At saturation point.			Satura-tion-pressure.	At one atmosphere.		S(sat.).
	Calories/deg.		Ratio.		Calories/deg.		
t.	S.	s.	g.	p.	S'.	Grindley.	Cal./deg.
° 0	0·4973	0·3866	1·2862	mm. 4·66	(0·6056)	(0·306)	−1·680
20	0·4984	0·3873	1·2870	17·67	(0·5758)	(0·308)	−1·502
40	0·5008	0·3885	1·2888	55·55	(0·5544)	(0·314)	−1·351
60	0·5055	0·3913	1·2921	149·63	(0·5416)	(0·326)	−1·223
80	0·5128	0·3952	1·2977	355·30	(0·5313)	(0·349)	−1·116
100	0·5236	0·4009	1·3060	760·00	0·5236	0·387	−1·028
120	0·5388	0·4090	1·3175	1491·4	0·5181	0·448	−0·955
140	0·5581	0·4188	1·3327	2716·5	0·5138	0·537	−0·895
160	0·5816	0·4303	1·3518	4657·0	0·5105	0·665	−0·844
180	0·6086	0·4427	1·3748	7546·0	0·5079	(0·827)	−0·801
200	0·6399	0·4568	1·4012	11684·0	0·5059	(1·043)	−0·759

Variation of the Total Heat and Latent Heat.

The Total Heat, H, of a vapour, defined in the usual manner, is related to the Latent Heat, L, by the simple equation

$$H = L + h \dots\dots\dots\dots\dots (29),$$

if the Heat of the Liquid h is reckoned from the same zero as the total heat of the vapour. In the case of water both H and h are reckoned from the state of water at 0° C. The specific heat of water is so nearly constant that h may often be taken as equal to t. More generally we may write

$$h = t + dh \dots\dots\dots\dots\dots (30),$$

where dh is the small difference of the heat h from the value t, which it would have if the specific heat were constant and equal to unity. According to the observations of Barnes, the variation of the specific heat is very nearly linear between 60° and 100° C. The value of h at temperatures above 60° C. may be taken as

$$h = t + dh = t + 0{\cdot}000110\,(t - 60)^2 \dots\dots\dots\dots (31).$$

This simple formula agrees very nearly with Regnault's observations in the rate of variation above 60°, and also with the table of values of h given by Callendar and Barnes.*

The accurate relation between the Total Heat and the Specific Heat of the Vapour is readily obtained by equating the intrinsic energy of steam evaporated at 0° C. at a pressure $p°$, and then heated at constant pressure $p°$ up to any temperature θ, to that of steam obtained by heating the liquid up to the same temperature θ, evaporating it at θ under the constant saturation pressure p, and expanding the vapour at constant temperature θ down to the pressure $p°$ of saturation at 0° C. The various changes of intrinsic energy involved in these processes are given by equations (20) and (22). After a few simple reductions we obtain the Equation of Total Heat,

$$\mathrm{H} - \mathrm{H}° = \mathrm{S}°(\theta - \theta°) - (n+1)(cp - c°p°) \dots\dots\dots\dots (32),$$

which is simply the expression of the first law of thermodynamics as applied to the problem, and might also have been obtained in various other ways. If we omit the small terms depending on the co-aggregation c, the equation is identical with that given by Rankine in 1850, on the assumption that saturated steam could be treated as an ideal gas. The small terms represent the effect of the deviations of steam from the ideal state, and become important at high pressures. The equation neglects the external work of expansion of the liquid, but this is less than one-thirtieth of a calorie at 200° C., although it may become important as the critical temperature is approached.

Equation (32) gives only the variations of the total heat of the saturated vapour. In order to find the absolute values, it is necessary to know the actual value of the total heat at some particular temperature. The obvious value to select would be that given by Regnault at 100° C., namely 637 calories. His methods do not appear, however, to have been sufficiently exact, and I prefer to rely on a more recent determination by Joly, with his steam calorimeter (described by Griffiths).† Joly determined the mean specific heat of water between 12° and 100° C in terms of the latent heat of steam at 100 C. Now the mean specific heat of water between 12° and 100° C. is known in terms of the specific heat at 20° C. by the results quoted above. We can therefore reverse the calculation, and find the latent heat of steam at 100° C. The result of the calculation gives L at 100° = 540·2 calories at 20° C. This is considerably in excess of Regnault's value, but it is quite within the limits of probable error of his experiments, and it possibly still errs in the direction of being too low. Assuming this value as a starting point, I have calculated the following table of

values of the total heat and latent heat, and of the rate of variation of the saturation pressure and the total heat with temperature, namely $dp/d\theta$ (sat.), and $dH/d\theta$. It will be observed that the rate of increase of the total heat diminishes rapidly at high temperatures, while the rate of diminution of the latent heat increases. This must necessarily be the case, as the latent heat should vanish near the critical temperature, which occurs about 365° C., according to the observations of Cailletet and Colardeau, whereas the linear formula of Regnault would make the latent heat vanish at about 870° C. This is an additional indication of the impossibility of Regnault's formula. It may be observed, however, that the average rate of increase of the total heat, according to Table III between 100° and 200° C., over the range of Regnault's experiments from which the linear formula (1) was calculated, is only 0·330 calorie per degree, which differs so little from the coefficient 0·305 given by Regnault as to be well within the limit of accuracy of his experiments, considering the acknowledged leakage of the distributing tap, and that the whole difference is only one-half of 1 per cent. on the quantity of heat measured.

The values of $dp/d\theta$, given in column 6 of the table, are calculated from those of L by means of the thermodynamic relation (3) already quoted, assuming the values of the specific volume from Table I.

Table III.—Total Heat and Latent Heat of Steam in terms of the Thermal Capacity of Water at 20° C.

Temp. cent.	$H - H°$ cals.	H. cals.	h. cals.	L. cals.	$dp/d\theta$. mm./deg.	$dH/d\theta$, cals./deg.	Regnault's formula.
0	0·00	593·5	0·00	593·5	0·3364	0·4935	606·5
20	9·83	603·3	20·06	583·2	1·089	0·4887	612·6
40	19·53	613·0	40·02	573·0	2·952	0·4800	618·7
60	28·99	622·5	60·00	562·5	6·904	0·4665	624·8
80	38·15	631·7	80·03	551·7	14·39	0·4467	630·9
100	46·83	640·3	100·14	540·2	27·164	0·4202	637·0
120	54·90	648·4	120·3	528·1	47·35	0·3885	643·1
140	62·32	655·8	140·6	515·2	77·06	0·353	649·2
160	68·9	662·4	161·1	501·3	118·62	0·314	655·3
180	74·9	668·4	181·6	486·8	173·50	0·274	661·4
200	79·9	673·4	202·3	471·1	243·0	0·237	667·5

The values of $dH/d\theta$ are obtained from those of $dp/d\theta$ by differentiating equation (32), thus,

$$dH/d\theta = S^\circ - (n+1)\,c\,(dp/d\theta - np/\theta).$$

It will be observed that the values of the total heat in the above table agree very closely with those of Regnault between 60° and 90°, where his results (according to Griffiths)[*] are most reliable. The average of his observations over this range is in exact agreement with Table III. At lower temperatures, Regnault's observations are very discordant, but the values given in the table are well supported by those of Griffiths. He finds, for instance, the latent heat to be $572\cdot7$ calories at $40\cdot2^\circ$ C., where the table would give $573\cdot1$. The unit employed by Griffiths (calorie at 15° C.) is different, so that his value would require to be raised nearly $0\cdot6$ cal. to reduce to the same unit, which would make it $573\cdot3$ calories at $40\cdot2^\circ$. There can be no doubt that his observations are entitled to much greater weight than those of Regnault, which are nearly 6 calories larger at this point. The value, $596\cdot7$ found by Dieterici with an ice calorimeter,[†] for the latent heat at 0° C., is $3\cdot2$ calories larger than that given in the table. But it must be remembered that observations of the latent heat at 0° C. are not at all easy, and that there is some uncertainty about the unit employed by Dieterici, as he finds by the same method the value of the mean specific heat of water between 0° and 100° C., about 1 per cent. larger than Reynolds and Moorby or Callendar and Barnes. It is possible that his result might agree with Table III if it could be reduced to the same units.

Entropy of Water and Steam.

The entropy of water, ϕ_w, is readily calculated from a table of the values of the specific heat when the variation of the specific heat is known. Since, however, the specific heat is nearly equal to unity, we may write,

$$\phi_w = \log_e \theta/\theta^\circ + d\phi \quad\dots\dots\dots\dots\dots\dots\dots (33),$$

where $d\phi$ is the small difference of the value at any temperature from the value $\log_e \theta/\theta^\circ$, calculated on the assumption of constant specific heat. The values of $d\phi$ given in the following table have been calculated from the table of values of the specific heat given by Callendar and Barnes.[‡] It will be seen that the values of $d\phi$ are very small at temperatures below 100° C., but increase rapidly at higher temperatures. Above 200° C. the values of the specific heat of water are so uncertain that it is not possible to calculate the properties of steam satisfactorily by any method. The values of $dh/\theta = (h-t)/\theta$ are also

* 'Roy. Soc. Proc.,' December, 1894.

† 'Wied. Ann.,' vol. 37, p. 504, 1899.

‡ 'Brit. Assoc. Rep.,' 1899.

given in the table for comparison with those of $d\phi$. They are calculated from the same table of the values of the specific heat, and the difference $d\phi - dh/\theta$ is seen to be small. This difference occurs as a small correction in the equation for the saturation-pressure, to be presently given. The values of the entropy of water, corrected for the variation of the specific heat are given in the column headed ϕ_w. The values of the entropy of steam are obtained by adding the values of L/θ given in the next column, which are found from the values of the latent heat already given in Table III. Values of ϕ_s, calculated from Regnault's formulæ, are given in the last column for comparison.

Table IV.—Entropy of Water and Steam.

t.	dh/θ.	$d\phi$.	$\mathrm{Log}_e \,\theta/\theta°$.	ϕ_w.	L/θ.	ϕ_s.	Regnault.
$°0$	0	0	0	0	2·1740	2·1740	2·214
20	0·00016	0·00017	0·07070	0·07087	1·9908	2·0617	2·089
40	0·00008	0·00009	0·13672	0·13681	1·8308	1·9676	1·982
60	0·00000	0·00001	0·19867	0·19868	1·6892	1·8880	1·890
80	0·00009	0·00010	0·25694	0·25704	1·5628	1·8198	1·814
100	0·00037	0·00039	0·31208	0·31246	1·4483	1·7608	1·748
120	0·00084	0·00090	0·36428	0·36518	1·3438	1·7090	1·692
140	0·00152	0·00163	0·41404	0·41567	1·2475	1·6632	1·644
160	0·00242	0·00261	0·46112	0·46373	1·1578	1·6215	1·604
180	0·00353	0·00384	0·50645	0·51029	1·0746	1·5849	1·568
200	0·00497	0·00532	0·54960	0·55492	0·9960	1·5509	1·536

The Entropy Equation.

By the application of the second law of thermodynamics we may obtain a relation between the latent heat and the saturation-pressure. Expressing the fact that the entropy of steam evaporated at $\theta°$, and heated at constant pressure $p°$ up to any temperature θ, is the same as the entropy of steam obtained by heating water up to the same temperature, θ, evaporating it at saturation-pressure, p, and then expanding it at constant temperature, θ, down to the pressure, $p°$, of saturation at $\theta°$, we immediately obtain the entropy equation

$$(1 - S°)\log_e \theta/\theta° + L/\theta - L°/\theta° + R \log_e p/p°$$
$$+ d\phi_w + ncp/\theta - nc°p°/\theta° = 0 \ldots\ldots (34).$$

The various terms of this equation have been already calculated, and are given in equations (18), (24), (26), and in Table IV. The last three terms of the equation are small, and represent the effect of the variation of the specific heat of water, and of the deviation of the properties of steam from the ideal state, as expressed by the characteristic equation (6). Neglecting the small terms, the equation is identical with one given by Bertrand, on the assumption that steam may be treated as an ideal gas. It is evident that the values of the saturation-pressure may be calculated from this equation by means of the values of the latent heat already found. It is better, however, to eliminate L by means of the energy equation (32) already given.

Equation of the Saturation-Pressure.

If we substitute $H - H° = L - L° + h = L - L° + t + dh$, in the energy equation (32), and divide by θ, and subtract from the entropy equation (34) above given, we obtain the equation of saturation-pressure, which may be reduced to the form

$$R \log_e p/p° = (L°/\theta° + np°c°/\theta°)t/\theta - (1 - S°)(\log_e \theta/\theta° - t/\theta)$$
$$+ (pc - p°c°)/\theta - (d\phi - dh/\theta) \ldots\ldots (35).$$

Neglecting the terms depending on the co-aggregation, and on the variation of the specific heat of water, this equation is equivalent to one given by Dupré and Bertrand, and rediscovered in various ways by many other observers (*e.g.*, Pictet and Hertz).[*] If the correct values of S°, L°, and R are inserted in the formula, the equation thus simplified gives very accurate values of the saturation-pressure at low pressures where the properties of steam satisfy approximately the fundamental assumptions made in deducing the formula. Bertrand,[†] although of course he was well aware that the formula thus obtained was not accurate at high pressures, has calculated numerical formulæ of this type for a large number of vapours, choosing the constants empirically so as to obtain the best agreement over the whole range. The values of the constants so found do not, of course, agree with the correct values of L° or S°. The numerical values chosen by Bertrand in the case of water, for instance, give $L° = 573$ calories, $S° = 0.575$ cal. per deg., and the value of the steam pressure found is 763 mm. at 100° C. At low temperatures the first term in formula (35) is the most important, since $\log_e \theta/\theta°$ is very nearly equal to t/θ when t is small. The formula then reduces to the simple type, $\log p = A + B/\theta$, which has often been employed for approximate work, and is the basis of the useful relation of Ramsay and Young.[‡] Adding a second term, C/θ^2, to this formula

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[*] Pictet, 'Comptes Rendus,' vol. 90, p. 1070, 1880 (proof invalid); Hertz, 'Wied. Ann.,' vol. 17, p. 177, 1882.

[†] 'Thermodynamique,' p. 93.

[‡] 'Phil. Mag.,' vol. 21, p. 33.

to take account of the small terms in equation (35), we obtain the well-known empirical formula of Rankine (1849), which is very convenient and accurate. A nearly equivalent formula is that of Unwin,* $\log p = A + B\theta^b$, in which the same effect is empirically secured by an arbitrary exponent. These formulæ are purely empirical, but it is interesting to observe how they are related to the correct thermodynamical expression (35).

Saturation-Pressures of Steam.

In employing equation (35) to calculate the numerical values of the saturation-pressure in the case of steam, we have only one empirical constant, namely, p°, which is determined by the condition that the saturation-pressure at 100° C. is 760 mm. The values of the other constants which occur in this equation have been already given, namely,

$S^\circ = 0·4966$ cal./deg. $L^\circ = 593·5$ cals. $R = 0·11037$ cal./deg.

The value of θ°, which is also one of the fundamental data, is taken as being 273°, but is uncertain to the extent of 0·1°. Dividing the equation by R, and reducing to common logarithms by the modulus $\log_e 10 = 2·3026 = m$, we obtain the numerical formula

$$\log_{10} p/p^\circ = 8·554t/\theta - 4·561F(\theta) + (pc - p^\circ c^\circ)/mR\theta$$
$$- (d\phi - dh/\theta)/mR \dots\dots (36).$$

in which $F(\theta)$ stands for the function $\log_{10} \theta/\theta^\circ - t/m\theta$. I have used this form for calculation, and have given the values of the separate terms in Table V so as to show their relative importance. It is also possible to write the formula in the shape, $\log p = A + B/\theta + C \log \theta + \text{small terms}$, but this does not show so clearly the relative effect and importance of L° and S°.

The values of the saturation-pressure in the column headed p are calculated by the complete thermodynamic formula (36). The values given in the column headed Regnault are those of Regnault, recalculated by Peabody and reduced to latitude 45°. The difference expressed in degrees of temperature is given in the last column, and is probably within the limits of error of Regnault's observations and of the empirical formulæ employed to represent them. If we refer to the actual observations of Regnault, we find that the discrepancies of individual observations at any point, expressed in degrees of temperature, exceed the values of the differences shown in the last column. We also find that in most cases the actual observations agree better with the single formula (36) than they do with the two empirical formulæ, each with five arbitrary constants, from which the values in the column headed

* 'Phil. Mag.,' vol. 21, p. 300.

Table V.—Saturation-Pressures of Steam.

$t.$	$8 \cdot 554t/\theta.$	$-4 \cdot 561\mathrm{F}(\theta).$	$+\dfrac{(pc-p^\circ c^\circ).}{m\mathrm{R}\theta}$	$-\dfrac{d\phi-dh/\theta}{m\mathrm{R}}$	$p.$	Reg-nault.	Diff.
$\overset{\circ}{0}$	0	0	0	0	4·66	4·60	$0\cdot\overset{\circ}{18}$
20	0·5838	−0·0049	+0·0003	0	17·68	17·40	0·26
40	1·0932	−0·0177	+0·0009	0	55·55	54·91	0·20
60	1·5413	−0·0367	+0·0020	0	149·63	148·80	0·12
80	1·9387	−0·0603	+0·0039	0	355·30	354·63	0·04
100	2·2932	−0·0872	+0·0066	−0·0001	760·00	760·00	0·00
120	2·6120	−0·1169	+0·0104	−0·0002	1491·4	1490·5	0·02
140	2·8998	−0·1488	+0·0152	−0·0005	2716·5	2717·9	0·02
160	3·1612	−0·1817	+0·0211	−0·0008	4657	4652	0·05
180	3·3990	−0·2163	+0·0279	−0·0012	7546	7537	0·05
200	3·6170	−0·2514	+0·0357	−0·0018	11684	11664	0·08

Regnault were calculated. Taken in conjunction with the differential throttling experiments, and with the direct measurement of the specific heat by the electrical method, this is very strong evidence that Regnault's formula for the total heat is incorrect, and that the values of the total heat and latent heat given in Table III, and supported by the experiments of Griffiths and Joly, should be accepted in its place.

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"Note on Inquiries as to the Escape of Gases from Atmospheres."
    By G. JOHNSTONE STONEY, M.A., Hon. D.Sc., F.R.S. Received
    and Read June 21, 1900.

We have now three investigations which profess to supply informa-
tion about the escape of gases from atmospheres. Two of them, those
of Messrs. Cook and Bryan, reason forward by the help of the kinetic
theory of gas from the supposed causes; the third, which is that pre-
ferred by the present writer, reasons backward by the help of the same
theory from the observed effects.

Mr. Cook's investigation, which will be found in the 'Astrophysical
Journal' for January, 1900, seeks to compute the proportion of mole-
cules which can attain the speed requisite for escape by means of the
formula which Maxwell published in 1860, assigning the proportion of